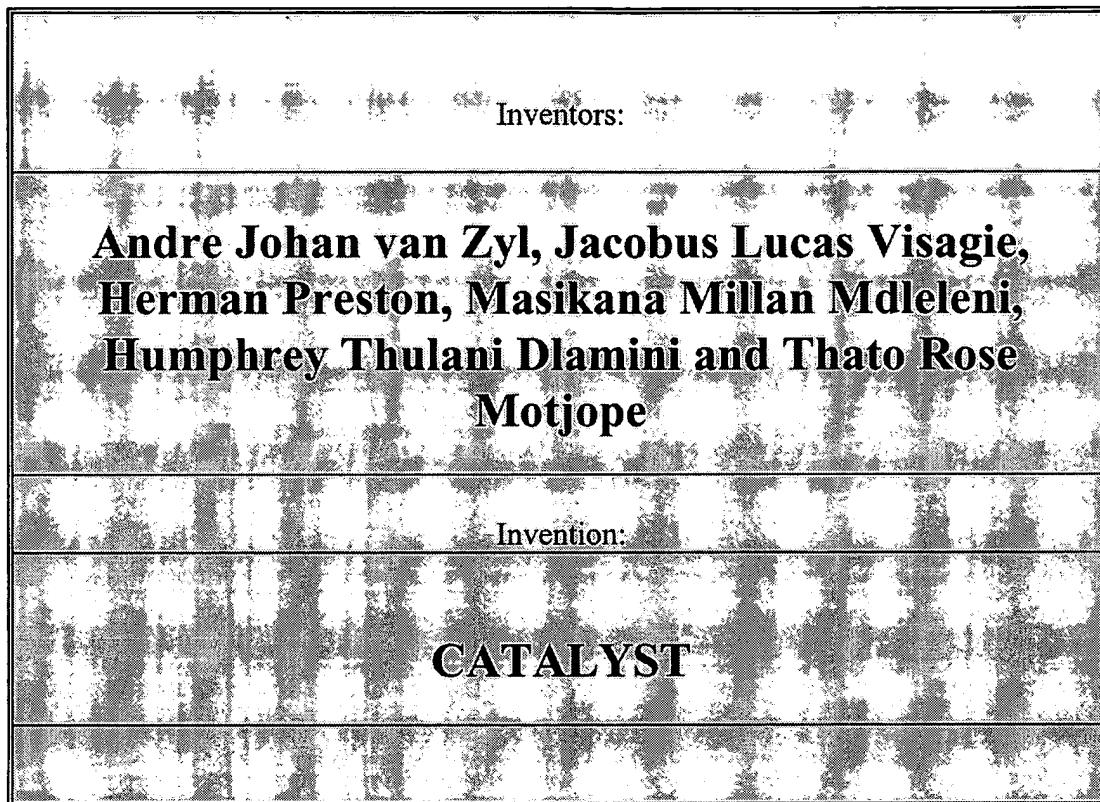


**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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- Utility Patent Specification -



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I, Sheri Cooper, hereby certify that this correspondence and all referenced enclosures are being deposited by me with the United States Postal Service as Express Mail with Receipt No. EV317506046US in an envelope addressed to: Commissioner for Patents:, on November 24, 2003.

## CATALYST

### BACKGROUND OF THE INVENTION

THIS invention relates to iron-based catalysts, in particular to iron-based catalysts and their use in the conversion of synthesis gas (CO and H<sub>2</sub>) to alcohols and olefins.

International patent publication no. WO 01/89689 discloses an iron-based Fischer-Tropsch catalyst composition wherein the iron phase is ferrihydrite. The catalyst composition includes natural promoters which may be selected from manganese or chromium or a mixture thereof and chemical promoters selected from magnesium zinc, copper and alkaline or alkali earth metals. The catalyst is best bound to refractory oxide support. The catalyst composition is formed by preparing a solution containing Fe ions and nitrates of Zn, Mn and Cu. This solution is reacted with a solution containing a base, such as KOH, to form a precipitate wherein the main iron phase of the precipitate is ferrihydrite. The precipitate is then washed, dried and bound with a refractory metal oxide. According to the specification, the catalyst composition produces significant yield of higher paraffins, olefins and alcohols.

It is an object of this invention to provide an improved method of producing an iron-based Fischer-Tropsch catalyst composition which has greater selectivity towards olefins.

## SUMMARY OF THE INVENTION

This invention relates to a method for producing an iron-based Fischer-Tropsch catalyst composition, the catalyst composition having a high olefin selectivity when used in a Fischer-Tropsch reaction.

According to the invention there is provided a method for producing an iron-based Fischer-Tropsch catalyst composition (typically a composition where the main iron phase is ferrihydrite) in a precipitation reaction of Fe ions in solution, wherein Fe(III) ions in solution are reduced to Fe(II) and thus the ratio of Fe(II)/Fe(III) in the solution is increased prior to precipitation of the catalyst. The ratio of Fe(II)/Fe(III) may be increased by introducing a stoichiometric amount of a reduction agent such as oxalic acid or formic acid to the solution during the catalyst preparation method.

By "iron-based" is meant that Fe makes up at least 30% (by mass) of the composition. The term "the main iron phase is ferrihydrite" means that at least 75% of the iron phase is ferrihydrite, as determined by X-ray diffraction using Co K alpha radiation. The preferred catalyst compositions exhibit hyperfine interaction parameters similar to those of ferrihydrite, as determined by Mössbauer absorption spectroscopy (MAS).

A "structural promoter" is a chemical species/element that helps to stabilise the ferrihydrite phase of the catalyst.

A typical method for preparing an iron-based catalyst pre-cursor wherein the main iron phase is ferrihydrite, includes the following steps:

1. preparing a first solution in a polar solvent, the solution containing Fe(III) ions and a reduction agent such as oxalic acid or formic acid to reduce Fe(III) ions to Fe(II) ions;

2. adding a precipitation agent, typically a base, to the solution to form a catalyst precipitate wherein the main iron phase is ferrihydrite;
3. washing the precipitate;
4. drying, typically spray-drying, the washed precipitate; and
5. calcining the dried precipitate.

The first solution may be formed by dissolving a ferric salt, such as Fe nitrate, in the polar solvent.

Typically, the ions of structural promoters such as Mn, Cu, Zn, Cd, Ni, Co, Al and chemical promoters such as Zn, Mg, Cu, Cr, Ru, Pd, Rh or and alkaline or alkali earth metals such as K, Na and La are included in the first solution.

Typically, the first solution includes iron nitrate, manganese nitrate, copper nitrate, zinc nitrate and aluminium nitrate.

The preferred base is KOH, however NaOH and Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> can also be used.

Preferably, the step 2 is carried out at a pH of 7-9, most preferably a pH of 8, and at a temperature of 50°C - 80°C, most preferably 68°C - 72°C.

According to a further aspect of the invention there is provided a method for producing higher paraffins, alcohols and particularly olefins selectively, by reacting hydrogen with carbon monoxide in the presence of a catalyst substantially as described herein above.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

**Figure 1** is a graph showing the crystallite size vs mole ratio of oxalic acid/Fe(III) catalysts prepared by using zero and different amounts of oxalic acid;

**Figure 2** is a graph showing the activities for catalysts prepared by using different amounts of oxalic acid;

**Figure 3** shows the alcohol selectivity for catalysts prepared using different amounts of oxalic acids; and

**Figure 4** shows the olefin selectivity of catalysts prepared using different amounts of oxalic acids

### **DESCRIPTION OF EMBODIMENTS**

This invention relates to a new method for producing an iron-based Fischer-Tropsch catalyst composition wherein the main iron phase is ferrihydrite in a precipitation reaction. It has been found that the reduction of Fe(III) species to Fe(II), and thus an increase in the Fe(II)/Fe(III) ratio, prior to precipitation affects the crystallite size of the crystallite particles of the catalyst, and enhances the olefin selectivity of the catalyst. The reduction of the Fe(III) species to Fe(II) can be attained *in situ* by the addition of a reduction agent (such as oxalic acid or formic acid) during the catalyst preparation method.

The catalyst composition of the invention may be produced in a continuous precipitation method by making a first acidic solution containing Fe nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Mn nitrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), Zn nitrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Cu nitrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , Al nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and a reduction agent in the form of oxalic acid, and heating the solution to 65°C. A second basic solution, containing 25%, by mass, KOH and at a

temperature of 45°C is then added to the first solution in a precipitation vessel. The rate at which the second solution is added to the first solution is adjusted so that the pH is maintained at a range of 7-9, preferably approximately 8 and the temperature at 50°C - 80°C, preferably approximately 68°C - 72°C. The addition of the second solution to the first solution causes the formation of a precipitate, which is the catalyst composition of the invention. The precipitate is then filtered, and washed and the filter cake then reslurried, optionally bound with SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, and spray-dried at an inlet temperature of 260°C and an outlet temperature of 120°C. Thereafter, on-spec catalyst is calcined at 450°C for 16 hours.

Table 1 below shows the elemental composition of a catalyst OLE 135A which was prepared using no oxalic acid, catalysts OLE 135B-G which were prepared using oxalic acid and catalyst OLE 135L which was prepared using formic acid. The percent oxalic acid is calculated in terms of Fe(III), i.e. 10% oxalic acid = 10 moles/100 moles Fe(III).

**Table 1**

Catalyst	% oxalic acid	Mole ratio of oxalic acid: Fe(III)	gZn/100g Fe	gMn/100g Fe	gCu/100g Fe	gK <sub>2</sub> O/100g Fe	gSiO <sub>2</sub> /100g Fe
OLE 135A	0	0	10.62	25.52	6.7	0.45	14.78
OLE 135B	20	0.2	10.84	24.35	6.97	1.37	8.09
OLE 135C	40	0.4	11.81	26.58	7.22	1.31	8.15
OLE 135D	60	0.6	10.98	22.76	6.22	1.09	9.74
OLE 135E	80	0.8	10.87	22.3	6.11	1.37	12.2
OLE 135F	100	1	10.18	18.16	5.16	2.02	11.74
OLE 135G	10	0.1	12.62	27.12	8.13	0.5	11.37
OLE 135L	10	0.1 formic acid	12.31	28.74	7.98	2.23	13.76

Table 2 below shows the surface area and pore volumes of the catalysts identified in Table 1 above.

**Table 2**

Catalyst	Surface Area m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /g
OLE A	95.78	0.40
OLE B	97.79	0.45
OLE C	75.34	0.42
OLE D	144.68	0.42
OLE E	125.38	0.45
OLE F	144.13	0.42
OLE G	102.6	0.47
OLE L	111.1	0.52

The catalyst composition according to the invention formed with a sufficient amount of a reduction agent is iron-based, the main iron phase is ferrihydrite, and the catalyst has a surface area of 100-300m<sup>2</sup>/g and a pore volume of 0.4 to 0.52.

The reduction agent partly reduces Fe(III) to Fe(II) causing a higher Fe(II)/Fe(III) ratio. This reaction is illustrated as follows:

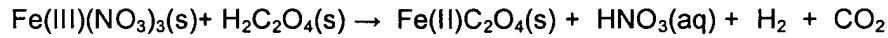


Figure 1 attached shows the mean crystallite size vs mole ratio of oxalic acid/Fe(III). As will be seen from Figure 1, it has been found that crystallite size of the catalyst increases with a decrease in the amount of oxalic acid added to the first solution. Table 2 shows that catalysts prepared with the introduction of 60% or more oxalic acid, (i.e. where the mole ratio of oxalic acid to Fe(III) is 0.6 or greater) have higher surface areas than the catalysts prepared with lower amounts of oxalic acid.

Catalysts prepared according to the invention were then tested. 20g of catalyst is loaded in a Fischer-Tropsch reactor in 350g molten wax, followed by in-situ reduction at 240°C, 20 bar and hydrogen gas hourly

space velocity of 6000ml(n)/g cat/hr for 16 hours. After reduction the temperature was lowered to 200°C and Arge Pure Gas (APG, approx. 75% syngas) introduced at 4500 syngas space velocity for one hour (This stage is known as catalyst conditioning. APG is introduced at a lower P & T and then gradually increased to synthesis conditions to avoid catalyst breakage). The temperature and pressure were then increased to 240°C and 45 bar respectively. After the first period analyses space velocities were adjusted to operate at 40% conversion. Gas samples were analysed by TCD (Thermal Conductivity detector is used to analysis for CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, Ar, N<sub>2</sub> (permanent gases)) and FID GC (Flame Ionisation detector is used to analyse all gaseous products (alcohols, paraffins, olefins, etc)) and the oils and water by FID GC (Flame Ionisation detector used to analyse liquid products (alcohols, paraffins, olefins, water, etc)) to calculate the product distribution.

Results of tests are shown in the attached Figures 2, 3 and 4. As can be seen from Figure 2, the amount of 10% to 40% reduction agent did not have a large negative effect on the activity of the catalyst. It will be seen from Figure 3 that the inclusion of from 10% to 40% reduction agent did not have a negative effect on the alcohol selectivity of the catalyst, with a slight increase in selectivity with the addition of 40%. Figure 4 however shows that the inclusion of more than 40% or more reduction agent leads to a large increase in the selectivity of the catalyst for olefins.

The invention will now be explained in more detail with reference to the following non-limiting Examples:

**Example 1. Preparation of OLE 135A-G**

Catalyst samples OLE 135A-G were prepared via the continuous precipitation method, where nitrates of Fe, Zn, Mn, Cu and oxalic acid were reacted with 25% KOH solution. The first step of preparation entailed the addition of various amounts of oxalic acid to the metal salt solutions heated to ~80 °C. The KOH solution was kept at ~ 45 °C. These two solutions were

then co-fed into the precipitation vessel. The rate at which these solutions were fed was adjusted such that the precipitation pH was ~ 8 and temperature was between 65 – 70 °C. After precipitation, the precipitates were filtered and washed to ~2 mS. The precipitates were then reslurried, bound with SiO<sub>2</sub> (10g/100g Fe). The final catalysts were spray dried at constant pump rate using the following conditions:

Inlet Temperature = 260 °C  
Outlet temperature = 120 °C  
Air flow = 65 % of maximum

Catalysts were calcined at 450 °C for 16 h.

The starting materials used for the preparation of these catalysts is presented in Table 3 and the final composition (mass%) is reported in Table 4.

**Table 3.** Raw materials of the preparation of OLE 135A-G

Catalyst	Raw materials used [g]						
	Fe nitrate	Zn nitrate	Mn nitrate	Cu nitrate	Oxalic acid	Silica sol 25% SiO <sub>2</sub>	25% KOH solution
OLE 135A	1787	143	399	68	0	90	1050
OLE 135B	1787	143	399	68	6.71	90	1050
OLE 135C	1787	143	399	68	13.4	90	1050
OLE 135D	1787	143	399	68	20.1	90	1050
OLE 135E	1787	143	399	68	26.8	90	1050
OLE 135F	1787	143	399	68	33.1	90	1050
OLE 135G	1787	143	399	68	3.36	90	1050

**Table 4.** Final elemental composition of OLE 135A-G (mass%)

Catalyst	%Fe	%Cu	%Mn	%Zn	%SiO2	%K <sub>2</sub> O
OLE 135A	46	3.08	11.5	5.06	11.6	0.21
OLE 135B	45	3.15	10.8	4.95	6.12	0.62
OLE 135C	45	3.15	11.7	5.31	6.12	0.59
OLE 135D	43	2.67	9.46	4.73	7.09	0.47
OLE 135E	43	2.63	9.46	4.73	8.77	0.59
OLE 135F	44	2.27	7.92	4.4	8.75	0.88
OLE 135G	44	3.52	11.9	5.54	8.45	0.22

**Example 2.** Use of an alternate reducing agent

For OLE 135L, formic acid with a mole ratio of 0.1 was used instead of oxalic acid. The preparation procedure was exactly as described in Example 1.

The starting materials used for this preparation is the same as that presented in Table 1 (for Fe, Cu, Mn, Zn and SiO<sub>2</sub>). The amount of formic acid used to obtain a mole ratio of 0.1 was 2.66g. This translated to ca. 0.06% (mole%).

The final composition of OLE 135L in mass % is presented in Table 5.

**Table 5.** Final elemental composition of OLE 135L(mass%)

Catalyst	%Fe	%Cu	%Mn	%Zn	%SiO2	%K <sub>2</sub> O
OLE 135L	36	2.88	10.4	4.43	8.42	36